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Vanadium Contamination and Associated Health Risk of Farmland Soil near Smelters throughout China

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Abstract

Whereas there is broad consensus that smelting causes serious soil contamination during vanadium production, little is known about the vanadium content of soil near smelters and the associated health risk at continental scale. This study is the first to map the distribution of vanadium in farmland soil surrounding smelters throughout mainland China, and assess the associated health risk. Analysis of 76 samples indicated that the average vanadium content in such soil was 115.5 mg/kg – far higher than the 82 mg/kg background content in China ($p < 0.05$). Southwest China (198.0 mg/kg) and North China (158.3 mg/kg) possessed highest vanadium contents. Vanadium content was strongly related to longitude, altitude, and atmospheric temperature. The reducible fraction accounted for the largest percentages in vanadium speciation. The average Pollution Load Index for all samples was 1.51, denoting significant metal enrichment. The Children's hazard index was higher than unity, indicating elevated health risk. The relative contribution of vanadium to the total health risk ranged from 6.02% to 34.5%, while nickel and chromium were the two main contributors in most regions. This work may serve as a model providing an overview of continental vanadium contamination around smelters, and draw attention to their possible health risks.

Keywords: Reducible vanadium; Soil contamination; Farmland soil; Smelter; Health risk assessment

1. Introduction

Vanadium is a strategically important metal that is widely used in modern society in the production of steel alloys and sulfuric acid (Zhang et al., 2009; Watt et al., 2018; Mikkonen et al., 2019). Vanadium resources occur worldwide in mineral and hydrocarbon deposits, with China, South Africa, and Russia the largest producers of vanadium products (Moskalyk and Alfantazi, 2003; Yu et al., 2019). Increasing demand for vanadium has promoted intensive mining and smelting activities (Zhang et al., 2018). For example, hundreds of vanadium smelters at different scales are distributed throughout the provinces of China (Yang et al., 2017). During vanadium processing, large quantities of vanadium-contaminated waste are discharged into the geochemical environment (Liu et al., 2017; Zhang et al., 2019b). Vanadium is a moderately toxic metal, which, if inhaled, can induce pulmonary tumors and increase the likelihood of lung cancer (Zhang et al., 2012; Jiang et al., 2018; Nedrich et al., 2018). Generally, vanadium exists in two oxidation states (tetravalent and pentavalent) in nature (Khan et al., 2011; Hao et al., 2015). Pentavalent vanadium is more toxic to plants, animals, and human beings than tetravalent vanadium because of its adverse influence on phosphate metabolism (Zhang et al., 2015).

During vanadium production, the smelting process causes the largest contamination (Imtiaz et al., 2015; Schlesinger et al., 2017). Vanadium waste discharged during smelting is usually deposited onto surface soil (Huang et al., 2015). For example, in Panzhihua, China, highest vanadium content of 4793.6 mg/kg is found in the surface soil for smelter sites among all processing stages of vanadium production, largely exceeding the soil background value of vanadium in China (82 mg/kg) (Cao et al., 2017). Vanadium can also migrate from soil to aquifer. Vanadium concentration up to 5.10 mg/L in groundwater has been found at a vanadium-bearing ore milling site in Rifle, Colorado, USA (Yelton et al., 2013), significantly higher than the notification level of 15 μg/L proposed by the California Office of Environmental Health Hazard Assessment. Moreover, farmland often surrounds vanadium smelters (Xiao et al., 2017). Given that food security and human health are directly affected by the quality of farmland soil (Rowell et al., 1998; Guan et al., 2019; Yang et al., 2019), pollution of such soil by nearby vanadium smelters is a subject of growing concern (Wang et al., 2018a; Shaheen et al., 2019). However, information is lacking on the vanadium content of farmland soil near vanadium smelters at continental scale, and the associated health risks.

In this work, the distribution of vanadium contents in farmland soils around smelters in China was described through analyzing 76 samples taken throughout the mainland. Vanadium speciation was examined to evaluate bioavailability. Their contaminant degree and health risk were also evaluated. Results from this work are helpful to reveal levels of vanadium concentration in farmland soil around smelters and raise concerns on their potential health issues previously ignored.

2. Materials and methods

2.1. Sample collection and chemical analysis

The total area of China was divided into 7 regions including Northeast China (NE), North China (NC), Northwest China (NW), Central China (CC), East China (EC), Southwest China (SW), and South China (SC) (Yuan and Luo, 2019). A total of 76 smelters were selected in July 2017, distributed with NE (9), NC (4), NW (9), CC (21), EC (17), SW (13) and SC (3), respectively. Approximately one-third of the total number of smelters in each region were included, with uniformly distributed locations. Each surface soil (upper 20 cm layer) sample was collected from farmland within 2-km distance of the smelter (Han et al., 2018). Every soil sample consisted of five homogenized subsamples collected at horizontal intervals of 50-80 m. Samples stored in polyethylene bags were delivered to the laboratory within 2 days and stored at 4 ^{o}C.

Before analysis, all collected farmland soils were air-dried, ground, and sieved through 2-mm mesh. 0.25 g soil samples with 100 meshes were digested with aqua regia (2 mL nitric acid, 5 mL hydrochloric acid, and 4 mL hydrofluoric acid) by a microwave digester (MARS 6, CEM Corp., USA) (Wang et al., 2020). The temperature was increased to 400 ^{o}C within 5 min, held for 10 min, then further increased to 1000 ^{o}C in 10 min, and maintained for 30 min. Finally, the temperature declined gradually to 50 ^{o}C. Vanadium and other metals were monitored with inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher X series, Germany). Vanadium speciation, including acid-soluble, reducible, oxidizable, and residual phases, was analyzed by the modified three-step Community Bureau of

Reference (BCR) sequential extraction method (Žemberyová et al., 2006). In short, soil samples were extracted by acetic acid, and the extract separated to obtain acid-soluble vanadium (Step 1). Then the solid residue of Step 1 was fed with hydroxylamine hydrochloride to acquire reducible vanadium in aqueous solution (Step 2). Afterwards, hydrogen peroxide was added to the solid residue of Step 2 to collect oxidizable vanadium in the extract (Step 3). Finally, the solid residue of Step 3 was retained for aqua regia digestion to obtain residue vanadium in extracted solution.

2.2. Calculation and assessment

Metal contamination was evaluated by Contamination Factor (CF) and Pollution Load Index (PLI) (Rinklebe et al., 2019). CF was defined as the ratio of specific metal content in our samples to its world-wide average value, different to the Enrichment Factor based on the standardization of a tested metal against a reference one with low occurrence variability (Gowd et al., 2010). CF < 1.0: low contamination; 1.0 ⩽ CF < 3.0: moderate contamination; 3.0 ⩽ CF < 6.0: considerable contamination; and CF ⩾ 6.0: very high contamination. PLI (unitless) was calculated by integrating all CFs in one overall contamination index. PLI > 1.0: significant contamination.

Universal indices were employed to assess health risk. Average Daily Dose (ADD) was calculated for three groups of persons: children, adult males, and adult females by considering metal content, soil ingestion rate, exposure frequency and duration, bodyweight, and averaging time (Jiang et al., 2017). Hazard Quotient (HQ, unitless) was the ratio of ADD to the oral reference dose of the specific metal. The sum of HQ values of all metals gave the Hazard Index (HI). HQ > 1.0 and HI > 1.0:

high health risk. All reference values and evaluation criterions were used as previously reported (Rinklebe et al., 2019). Statistical analysis was performed with a one-way ANOVA using the software program PAST.

3. Results and discussion

3.1. Vanadium distribution and speciation

Vanadium was detected in all sampled farmland soils around smelters throughout China (Fig. 1a). Average vanadium content was 115.5 ± 121.1 mg/kg (n = 76), higher than 82 mg/kg background vanadium content in soil ($p < 0.05$) (Cao et al., 2017). This value was also significantly higher than vanadium contents in topsoil from the USA (80 mg/kg) ($p < 0.05$) and Europe (68 mg/kg) ($p < 0.01$) (Gao et al., 2017). During smelter operations, dust clouds containing vanadium were discharged and became deposited on the soil, contributing to the high occurrence of vanadium in farmland soil (Chen and Liu, 2017). The two regions possessing the highest contents of vanadium were SW and NC, with average values of 198.0 ± 231.9 mg/kg (n = 13) and 158.3 ± 110.0 mg/kg (n = 4), respectively, both of which are abundant in vanadium resource and contain many plants for its intensive processing (Moskalyk and Alfantazi, 2003). Correlation analysis indicated that vanadium content was strongly related to geographical and meteorological parameters, especially longitude, altitude, and atmospheric temperature (Fig. S1, Supporting Information). Besides vanadium, raised levels of other metals such as nickel, chromium, and zinc were detected (Table

S1, Supporting Information). These metals were likely derived from minerals used in vanadium smelting (Zhang et al., 2020b), indicating that the surrounding farmland soil was experiencing contamination by a combination of different metals. Similar multiple-metal pollution during vanadium smelting was commonly found worldwide, an example being the Rifle site, Colorado, USA (Liang et al., 2012).

The reducible fraction accounted for the largest percentages in vanadium speciation (Fig. 1b), unlike previous studies which found that vanadium existed mainly as the residual fraction in smelting site soils (Zhang et al., 2019b). The present finding indicates that agricultural cultivation activities, including intensive irrigation, land inundation, and frequent plowing, enhance the mobility of vanadium dust particles, as vanadium waste experiences alternating wet/dry and oxic/anoxic conditions (Shaheen et al., 2016). This suggests that vanadium in farmland soils has high bioavailability (Song et al., 2018), which is a matter of environmental concern.

3.2. Contamination evaluation and health risk assessment

Average CFs of vanadium in most regions were less than 1.0, suggesting low contamination (Fig. 2). However, average CFs of vanadium in SW and NC were 1.53 and 1.23, respectively, higher than 1.0, implying moderate contamination due to relatively higher vanadium contents in these regions. The maximum CFs of vanadium were 6.45 and 3.77 in SW and CC, having accounted for the very high contamination and considerable contamination correspondingly. Besides vanadium, some coexisting metals possessed higher average CFs (Fig. 2). In particular, very high or considerable contamination was found in all regions except SC for nickel. Lead reached very high degree of concentration while chromium achieved considerable concentration in SW, indicating relatively heavy contamination. These contamination levels were similar to that found in a mixed type industrial area (Pathak et al., 2015).

The average value of PLI for all samples based on the CF values was 1.51, with that in SW (2.40) substantially higher than in other regions (Fig. 3). PLI values above 1.0 denote significant soil enrichment by metals. Cases of multi-metal contamination occurred in areas with long histories of smelting activities, concurring with previous observations by Antoniadis et al. (2017a). Enrichment was promoted by the wide spectrum of different metals present; Rinklebe et al. (2019) report similar behavior of toxic elements in soils that suffered industrial contamination along a river in Germany. Notably, significant contamination at a specific site with higher PLI values was found in SW, which therefore requires urgent risk management and possible remediation.

Average HQs of vanadium for children in all regions were lower than 1.0, with two highest values occurring in SW (0.52) and NC (0.40) (Fig. 4), indicating low probability of the occurrence of adverse health effects (Rinklebe et al., 2019). Average HQs of vanadium for two adult groups, male and female persons, were normally an order of magnitude lower than those for children in each region, suggesting that children were more sensitive than adults to metal contamination, which was consistent with results from risk evaluation for metals in a river basin (Singh and Kumar, 2017). Meanwhile, other metals with higher average HQs were also found (Fig. 4). For instance, average HQs of chromium in all regions were higher than 1.0 for children with the maximum value of 4.81 in NE, while average HQs of lead and nickel were also above 1.0 in most cases. These results confirmed that health risks associated with "soil-to-human" pathways through direct dust inhalation by humans were significantly high for more toxic metals released during vanadium smelting (Carlin et al., 2016).

The resultant average HIs for children in all regions based on the HQs were above 1.0, with maximum values of 9.61 in SW and 7.35 in NE (Fig. 5a), indicating elevated health risk. The average value of HI for children in all areas related to the present soil samples was 5.20, similar to 6.11 for children in areas where the soil was affected by lead-zinc smelting (Jiang et al., 2017). By contrast, the average HI values for adults in all regions were invariably less than 1.0 and lower than the corresponding levels for children. Similar trends were also reported by Lozowicka et al. (2016), indicating that children are more vulnerable than adults to ingestion exposure to dust with elevated metal content.

The relative contribution of vanadium to total health risk varied among the 7 regions, ranging from 6.02% to 34.5% (Fig. 5b). Although the highest content of vanadium was found from SW and NC, the highest percentage contribution of vanadium occurred in SC (34.5%). Nickel and chromium accounted for the two largest percentage metal contents in samples from most regions, with the value for nickel reaching 54.0% in NC and that for chromium 49.9% in SC. Nickel and chromium might originate from raw minerals and/or coal fuels for vanadium smelting (Chen et al., 2011). The contribution order for these common metals is similar to previous findings for industrial-contaminated soils (Antoniadis et al., 2017b).

3.3. Environmental implications

This work reveals, for the first time, the occurrence of high levels of vanadium concentration in farmland soil near smelters at the continental scale of mainland China. Vanadium contamination took place at varying degrees, especially in SW and NC regions of China. Combined pollution with multiple metals was commonly detected. Contamination indices suggested significant enrichment of metals in most situations. Health indices implied elevated health risk, especially for children. Results from the present work draw attention to farmland soil contamination caused by vanadium smelting. Furthermore, specific factors such as types of kilns were found to be positively related to vanadium contents, which could be employed as a guidance to control vanadium release into environment.

When entering farmland soil, vanadium could interact with organisms (Hao et al., 2018). The microbial community could be significantly affected by vanadium, while microbes could change the mobility and toxicity of vanadium (Zhang et al., 2015; Wang et al., 2018b; Zhang et al., 2019a). Uptake of vanadium by crops could also occur, affecting product quality (Tian et al., 2014; Imtiaz et al., 2017). Phytoremediation could be thereby conducted by selected hyperaccumulating plants (Aihemaiti et al., 2019). These influences and applications require further investigation. Furthermore, transfer of highly toxic and mobile vanadium (V) to less toxic and readily precipitated vanadium (IV) by microbes has proved promising for vanadium detoxification (Zhang et al., 2019a; Yelton et al., 2013; Zhang et al., 2020a). This bioremediation is worth testing for future implementation on vanadium-contaminated farmland soil around smelters.

4. Conclusions

Vanadium contents above background value in China (82 mg/kg) are commonly found in farmland soil surrounding smelters throughout mainland China, where the national average value is 115.5 ± 121.1 mg/kg (n = 76). Southwest China and North China possessed highest vanadium contents, with average values of 198.0 ± 231.9 mg/kg (n = 13) and 158.3 ± 110.0 mg/kg (n = 4), respectively. Vanadium content is strongly related to longitude, altitude, and atmospheric temperature. The reducible fraction with high bioavailability is the main vanadium speciation. Significant enrichment of metals is found for all samples with average PLI of 1.51. Children's hazard index is higher than unity, indicating elevated health risk. The relative contribution of vanadium to the total health risk ranges from 6.02% to 34.5%, while nickel and chromium are the two main contributors in most regions. The findings highlight potential health risks posed by vanadium waste in areas where smelters are located near farmland, which have been ignored to date.

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Figure captions.

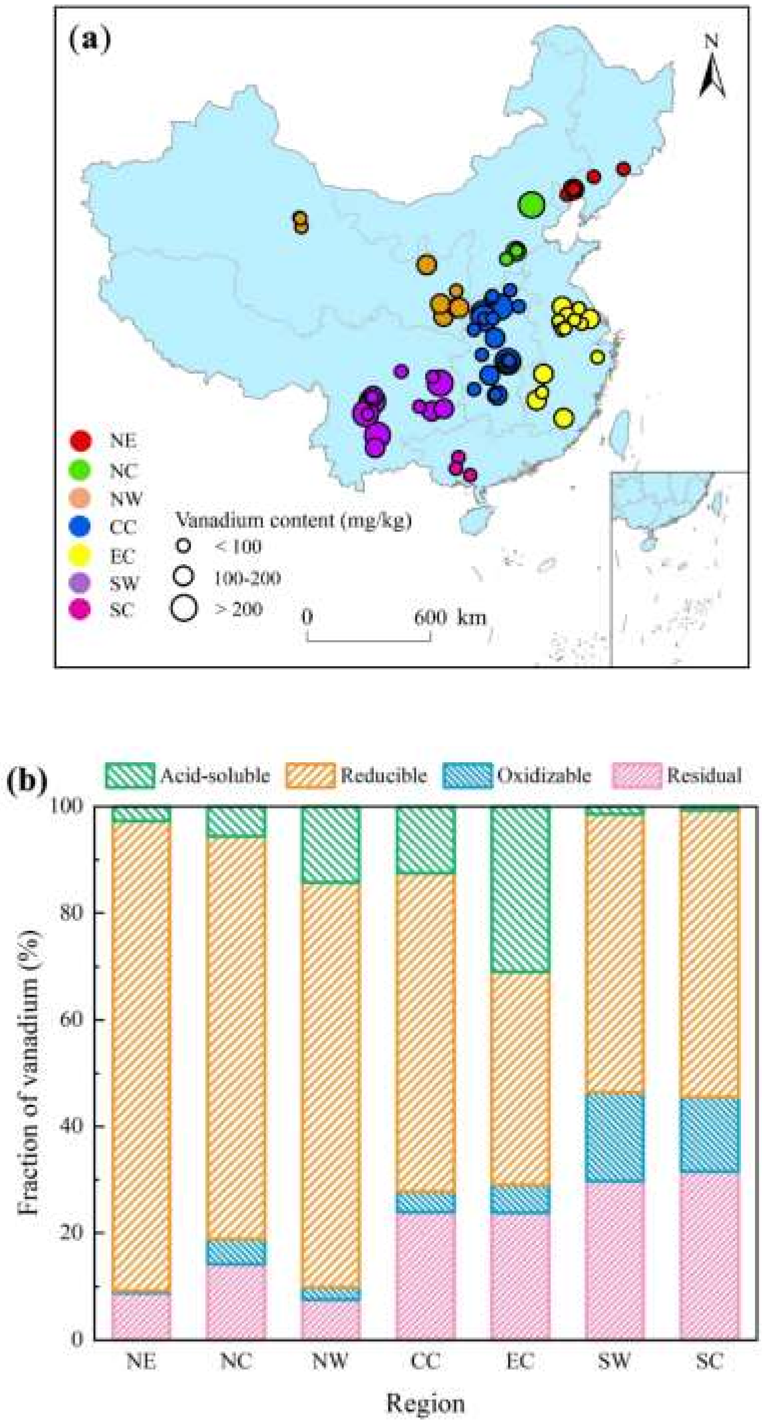
Fig. 1. Distribution and speciation of vanadium in farmland soil in the vicinity of vanadium smelters throughout China. (a) Vanadium distribution; (b) Vanadium speciation. NE: Northeast China; NC: North China, NW: Northwest China; CC: Central China; EC: East China; SW: Southwest China; and SC: South China.

Fig. 2. Contamination Factor (CF) of all metals in farmland soils around 76 vanadium smelters in 7 regions of China. (a) Vanadium; (b) Zinc; (c) Chromium; (d) Copper; (e) Lead; (f) Nickel. NE: Northeast China; NC: North China; NW: Northwest China; CC: Central China; EC: East China; SW: Southwest China; SC: South China. Red lines indicate the divisions in CFs at 1.0, 3.0 and 6.0. $CF < 1.0$: low contamination; $1.0 \leqslant CF < 3.0$: moderate contamination; $3.0 \leqslant CF < 6.0$: considerable contamination; and $CF \geqslant 6.0$: very high contamination.

Fig. 3. Pollution Load Index (PLI) of farmland soils around 76 vanadium smelters in 7 regions of China. NE: Northeast China; NC: North China, NW: Northwest China; CC: Central China; EC: East China; SW: Southwest China; SC: South China. The red line denotes the threshold above which soil is significantly enriched by metal.

Fig. 4. Hazard Quotient (HQ) of adult males, adult females and children of the health risk assessment of metals in farmland soils around 76 vanadium smelters in 7 regions of China. (a) Vanadium; (b) Zinc; (c) Chromium; (d) Copper; (e) Lead; (f) Nickel. NE: Northeast China; NC: North China; NW: Northwest China; CC: Central China; EC: East China; SW: Southwest China; SC: South China. The red line shows the level of $HQ = 1.0$, above which adverse health risks are high.

Fig. 5. Hazard Index (HI) used for health risk assessment and relative contributions of Hazard Quotients (HQs) in HI for metals in farmland soil samples taken in the vicinity of 76 vanadium smelters in 7 regions of China. (a) HI for adults and children; (b) Percentage of HQs in HI. NE: Northeast China; NC: North China, NW: Northwest China; CC: Central China; EC: East China; SW: Southwest China; and SC: South China.



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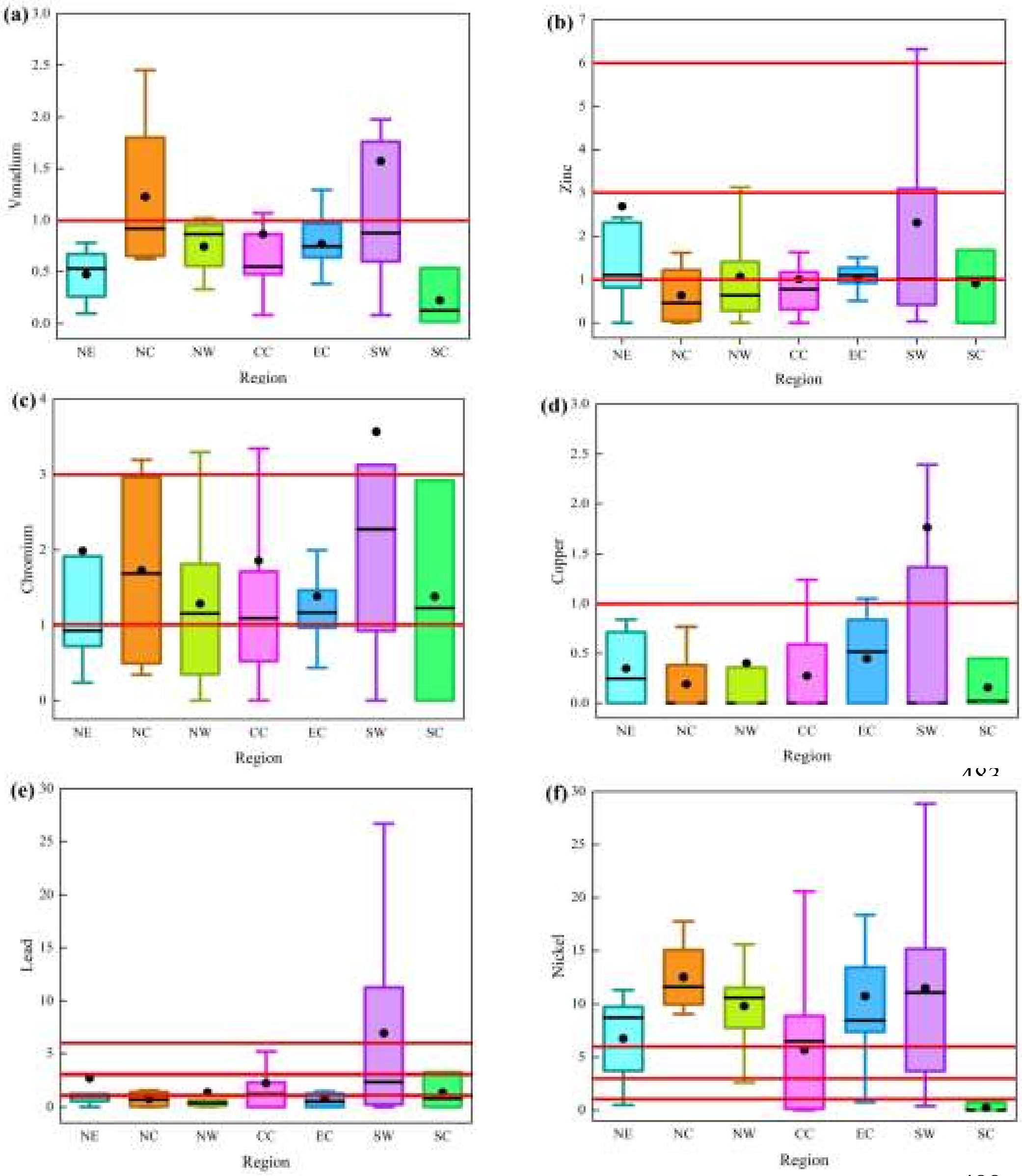

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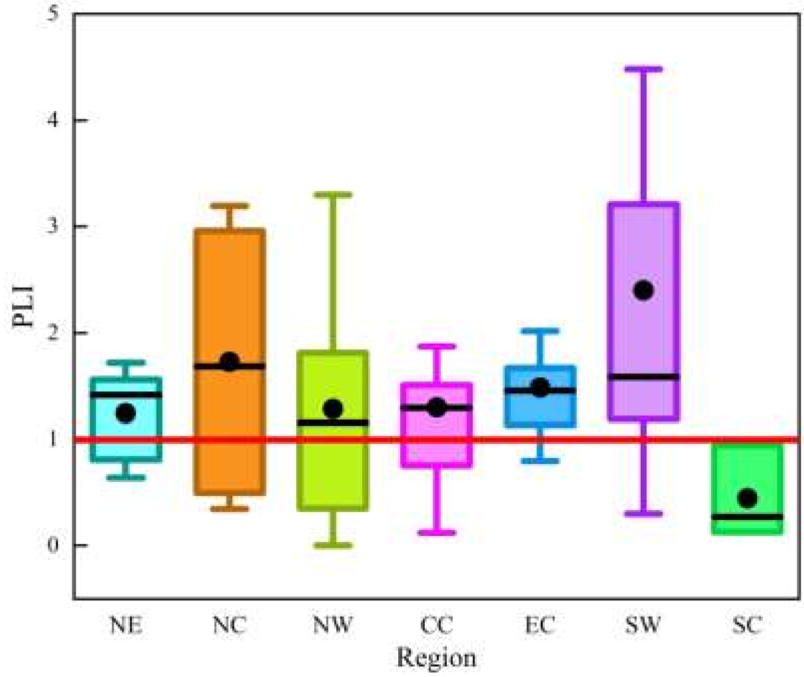

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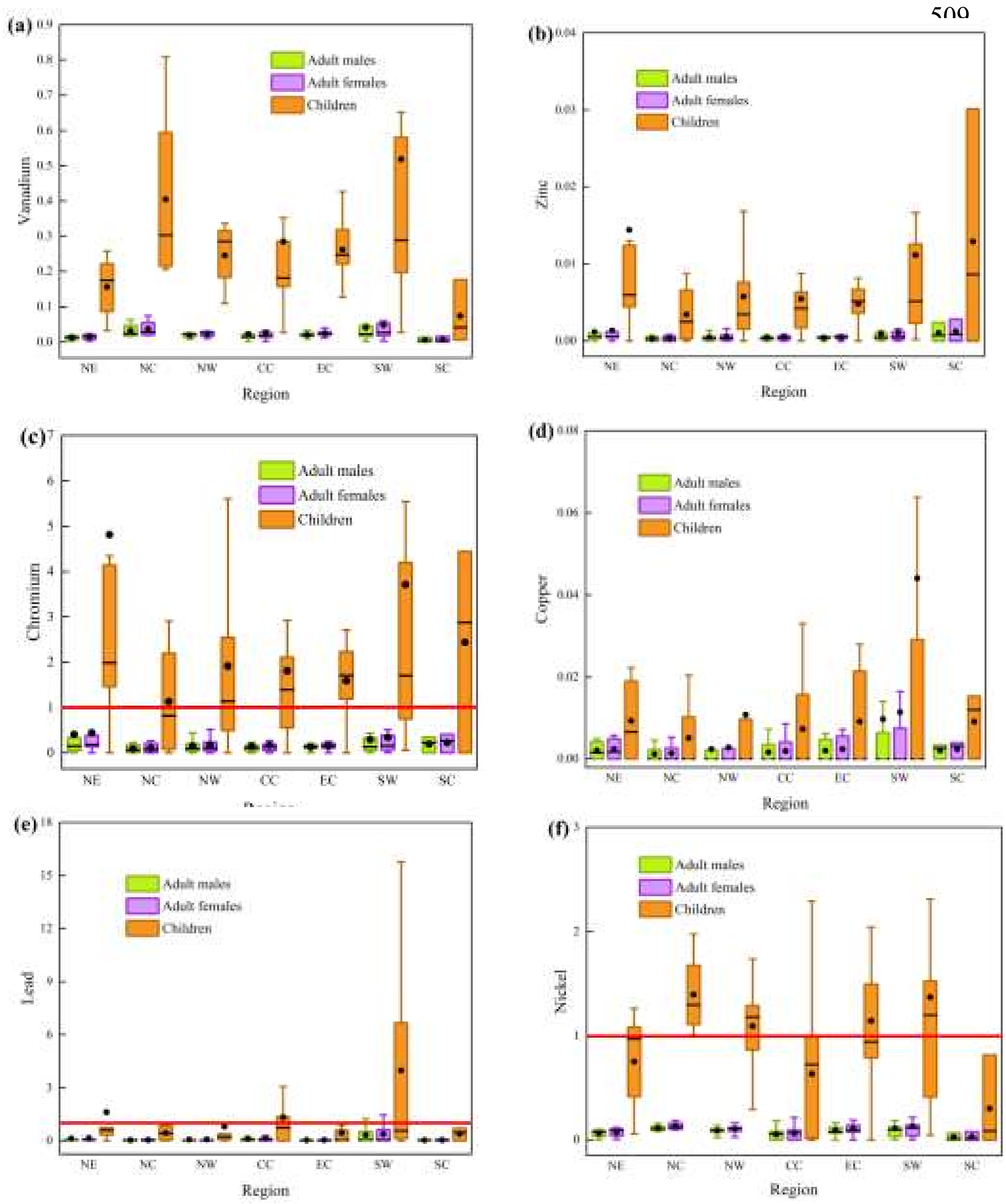

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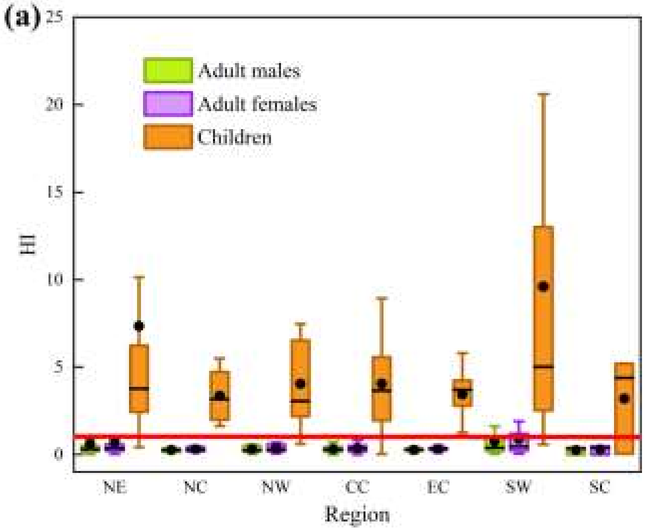

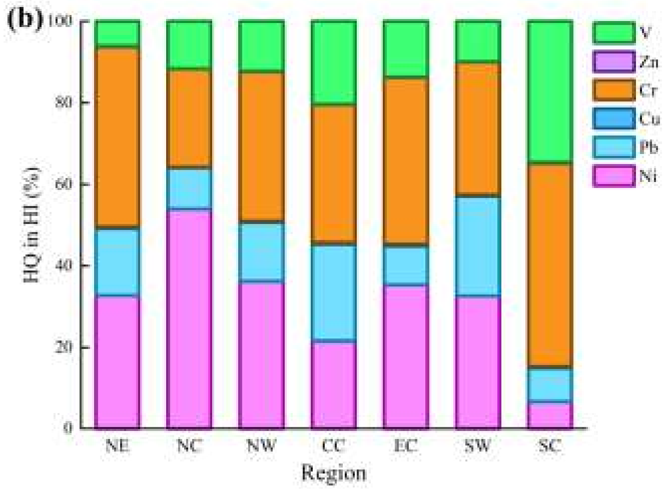

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